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Abstract

This report evaluates the large body of work involving the decomposition of PETN and identifies the major decomposition routes and byproducts. From these studies it becomes apparent that the PETN decomposition mechanisms and the resulting byproducts are primarily determined by the chemical environment. In the absence of water, PETN can decompose through the scission of the O-NO^2 bond resulting in the formation of an alkoxy radical and NO_2. Because of the relatively high reactivity of both these initial byproducts, they are believed to drive a number of autocatalytic reactions eventually forming $(NO_2OCH_2)_3CCHO$, $(NO_2OCH_2)_2C{=}CHONO_2$, $NO_2OCH{=}C{=}CHONO_2$, $(NO_2OCH_2)_3C\text{-}NO_2$, $(NO_2OCH_2)_2C(NO_2)_2$, $NO_2OCH_2C(NO_2)_3$, and $C(NO_2)_4$ as well as polymer-like species such as di-PEHN and tri-PEON. Surprisingly, the products of many of these proposed autocatalytic reactions have never been analytically validated. Conversely, in the presence of water, PETN has been shown to decompose primarily to mono, di, and tri nitrates of pentaerythritol.

Background

Pentaerythritol tetranitrate (PETN) [78-11-5] is an important high explosive (HE) and pharmaceutical belonging to the nitrate ester class of organic compounds. Some relevant physical properties of this class of explosives are given in **Table I**. PETN is the least reactive and most thermally stable of the nitrate ester explosives.[1] Visually, PETN appears as white crystals, and in its most stable form assembles into a tetragonal structure (i.e., space group P-bar-42_1c) with four molecules per unit cell. Two other commonly identified crystal habits include (1) "needle" or "hour glass" formations, having reentrant cavities from the ends and/or a high length-to-width ratio, and (2) "superfine" formations composed largely of irregular plates.[2] PETN's mechanical properties are quite interesting, exhibiting a strong directional dependence to shock initiated detonation. Although PETN is classified as quite easily detonated by shock, several directions of impact with respect to the crystal structure exist that will not cause

1 Lindner, V. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J.I.; Howe-Grant, M., Eds.;Wiley, New York, 1994; Vol. 10, p. 22.
2 Rogers, R.N.; Dinegar, R.H. "Thermal Analysis of Some Crystal Habits of Pentaerythritol Tetranitrate"; *Thermochim. Acta* **1972**, *3*, 367–378.

detonation, even when the shock wave fully crosses the crystal. Researchers have found that shock-initiated detonation occurs along the a-axis of the crystal but not along the c-axis.[3]

PETN is soluble in acetone [67-64-1], sparingly soluble in alcohols and ethers, and practically insoluble in water (1.5 μg/ml).[4] PETN has an extremely low vapor pressure at ambient temperatures and a tendency to adhere to surfaces.[5] This makes it difficult to maintain a stable vapor density of the pure material, which is desirable for a technique such as gas chromatography (GC).[6] Furthermore, raising the temperature to increase the vapor pressure accelerates the decomposition rate of PETN as observed by monitoring the emission of gaseous byproducts. The decomposition rate increases appreciably at temperatures over 100 ^{o}C.[5]

Table I. Properties of PETN

Property	**Value**[3,4,7,1]
color	colorless
crystal form	tetragonal
solubility in H_2O at 20 °C	1.5 μg/ml
molecular weight	316.15
density	1.76 g/cm^3
melting point	141.3 °C
vapor pressure at 97 °C	0.0011 mbar
weight loss at 100 °C	1 %
explosion temperature at 5 s	225 °C
detonation temperature	3400 K
activation energy	47.08 kcal/mol
heat of formation	0.41 kcal/g
heat of combustion	1.96 kcal/g
heat of detonation	1.50 kcal/g

The literature on PETN decomposition activation energy values, E_A, has been reviewed and reveals a range of values falling between 30 and 70 kcal/mol.[8] In contrast, the average RO-NO_2

3 Zaoui, A.; Sekkal, W. "Molecular Dynamics Study of Mechanical and Thermodynamic Properties of Pentaerythritol Tetranitrate"; *Solid State Commun.* **2001**, *118*, 345–350.

4 *The Merk Index*; Budavari, S., Ed.; Merck: Rahway, NJ, 1989; p 7068.

5 Eiceman, G.A.; Preston, D.; Tiano, G.; Rodriguez, J.; Parmeter, J.E. " Quantitative Calibration of Vapor Levels of TNT, RDX, and PETN Using a Diffusion Generator with Gravimetry and Ion Mobility Spectrometry"; *Talanta*, **1997**, *45*, 57–74.

6 Janni, J.; Gilbert, B.D.; Field, R.W.; Steinfeld, J.I. "Infrared Absorption of Explosive Molecule Vapors"; *Spectrochim Acta Part A,* **1997**, *53,* 1375–1381.

7 Köhler, J.; Meyer, R. *Explosives*, 4th ed.; VCH: New York, 1993, p. 271.

bond energy in nitrate esters is 40.7 ± 2 kcal/mol.[9] This range is attributed to the complex decompositional nature of PETN juxtaposed with the diversity of methods used to determine the energy of activation.

PETN as an Explosive

PETN has an endothermic initial step of ignition, which accounts for its stability at room temperature. However, ignition is a multi-phase process that progresses to self-sustained exothermic reactions. This characteristic is also common to all HE. Although the transition zone from slow thermal decomposition to violent explosion has been studied in PETN using laser pyrolysis and mass spectrometry (MS), the reaction mechanisms are still not well understood.[10]

PETN is used in several formulations and a few of the more common ones are summarized in **Table II**. Detasheet (Du Pont de Nemours) is a commercial formulation comprised of 63% PETN and 8% nitrocellulose mixed with a plasticizer.[11] PETN is also incorporated into a fabric that is then rolled into a fuse cord sometimes called Detacord. Both Detasheet and Detacord are important to industries involved in blasting such as mining and construction.

PETN is also a major component of the plastic explosives SEMTEX-1A and SEMTEX-H, which are made in Czechoslovakia.[12] Analysis of SEMTEX residue has become increasingly important because it is frequently used by terrorists.[13] The SEMTEX–1A formulation is comprised of 83.5% PETN, 12.4% oil, 4.1% styrene-butadiene rubber binder, and 0.002% dye (Sudan IV). The SEMTEX-H formulation consists of a minimum of 25% PETN, a maximum of 65.5% (cyclo-1,3,5-trimethylene-2,4,6-trinitramine) RDX for a combined total of 85.5%, 11.6% oil, 2.9% styrene-butadiene rubber binder, and 0.002% dye (Sudan I). However, quality control

8 Van der Merwe, M.; Fouché, F.C.; Von Abo, M. 17th Int. Ann. Conf. ICT, Fraunhofer Institut für Chemische Technologie (ICT): Karsruhe, Germany, 1986, p 62-1.

9 Batt, L.; Robinson, G.N. *Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives, Part 2*; Patai, S. Ed.; Wiley: Chichester, England, 1982, Chapter 24.

10 Östmark, H.; Bergman, H.; Ekvall, K. "Laser Pyrolysis of Explosives Combined with Mass Spectral Studies of the Ignition Zone"; *J. Anal. Appl. Pyrolysis,* **1992**, *24*, 163-178.

11 Huang, C.C.; Ger, M.D.; Lin; Y.C.; Chen, S.I. "Thermal Decomposition of Mixtures Containing Nitrocellulose and Pentaerythritol Tetranitrate"; *Thermochim. Acta,* **1992**, *208*, 147–160.

12 Mostak, P. "The Application of Plastic Explosives in Civil Blasting Techniques"; VSHZ Synthesia, unpublished report, pp 1-9.

13 Feraday, A.W. In *Advances in Analysis and Detection of Explosives*; Yinon, J. Ed.; Kluwer Academic Publishers: Dordrecht, Netherlands, 1992, pp 67-72.

for the SEMTEX formulations is frequently in question. Various lots have been found to be contaminated with other explosives, dyes, plasticizers, and a number of organic compounds.[14]

Table II. Common and Relevant Formulation of PETN

	Formulation	
Name	**PETN**	**Binder**
Detasheet	63%	8% nitrocellulose
SEMTEX-1A	83.5%	4.1% styrene-butadiene rubber 12.4% oil
SEMTEX-H	Min. 25% PETN (Max. 65.5% RDX) 85.5% Total HE	2.9% styrene-butadiene rubber 11.6% oil
LX-16	96%	4% chlorofluoropolymer (Oxy 461)
XTX8003	80%	20% polysiloxane (Sylgard 182)

PETN in Forensics

SEMTEX-H is frequently used in terrorist activities and consequently forensic scientists find the identification of PETN in post-explosion debris helpful for assigning culpability.[15] During an explosive event, not all energetic material is consumed.[16] Some of the material is volatilized in the extreme heat of the explosion, and then condensed on the cooler objects in the debris. In contrast, the end products of fully exploded material are usually simple salts (such as carbonates), water and carbon dioxide. These compounds are shared in common by most explosive materials, thus making them useless as specific identifiers.[17] Therefore, the detection and analysis of the condensed undetonated residues are particularly important in the investigation of a crime scene. The undetonated residues may consist of not only the explosive material itself but also the decomposition products and intermediates. This makes the identification of the decomposition products and intermediates of PETN important.

14 Hobbs, J.R. In *Advances in Analysis and Detection of Explosives*; Yinon, J. Ed.; Kluwer Academic: Dordrecht, Netherlands; 1992; pp 409-427.
15 Yinon, J.; Zitrin, S. *The Analysis of Explosives*; Pergamon Press: Oxford, 1981.
16 Steinfeld, J.I.; Wormhoudt, J. "Explosives Detection: A Challenge for Physical Chemistry"; *Ann. Rev. Phys. Chem.* **1998**, *49*, 203-32.
17 Basch, A.; Margalit, Y.; Abramovich-Bar, S.; Bamberger, Y.; Dalia, D.; Tamiri, T.; Zitrin, S. "Decomposition Products of PETN in Post Explosion Analysis"; *J. Ener. Mater.* **1986**, *4*, 77–91.

In 1986, the Israeli National Police noted that the thin layer chromatography (TLC) of post-explosion debris from a PETN-based explosive contained more compounds that reacted to a Griess reagent than the PETN itself. It was proposed, and later proved, that these compounds were the lower nitrate esters of pentaerythritol (PE) [115-77-5]. MS and NMR were used to find and isolate the hydrolysis products, pentaerythritol dinitrate (PE-di-N) [1607-01-8] and pentaerythritol trinitrate (PE-tri-N) [1607-17-6]. A third compound remained unidentified from the liquid chromatogram of the debris extract. It is tempting to speculate that this third peak is due to a third hydrolysis product of PETN, pentaerythritol mononitrate (PE-mono-N) [1607-00-7]. Unfortunately, PE-mono-N could not be used as a comparative standard in the research because it could not be isolated from the synthetic mixture. PE-mono-N as a PETN post-explosion analyte is yet to be established.[17]

PETN as a Pharmaceutical

PETN is also an important pharmaceutical used as a potent vasodilator in the treatment of angina pectoris and ischemia of the skeletal muscles. It falls within the same therapeutic class as nitroglycerine (NG), the drug of choice for acute cases of the above maladies.[18] However, PETN has a slower onset of action and, thus, a longer duration making it well-suited for prevention but not for the treatment of attacks. It is routinely mixed with lactose to prevent its detonation.

PETN was first synthesized as a pharmaceutical in 1895 and hence, its development as a drug occurred at a time when chemical analytical methods were not as sophisticated or sensitive as they are today. For this reason, information on pentaerythritol tetranitrate pharmacokinetics lags behind other drugs. Nevertheless, the major metabolites of ^{14}C-PETN have been studied in rats, mice, and humans. In 1997, PETN and its metabolites were studied in human plasma by extraction into dichloromethane and analysis by GC/MS.[19] The metabolites found were PE-mono-N, PE-di-N, and PE-tri-N.

Although, considerable interest in the shelf life of PETN tablets exists, current research has focused on the amount of pure material remaining in an aged dosage form and not the identification of the decomposition products. This could be attributed in part to the use of simple

18 Olsen, C.S.; Scroggins, H.S. "High-Performance Liquid Chromatographic Determination of the Nitrate Esters Isosorbide Dinitrate, Pentaerythritol Tetranitrate, and Erythrityl Tetranitrate in Various Tablet Forms"; *J. Pharm. Sci.* **1984**, *73*, 1303–1304.

instrumentation like stand alone chromatography and simple spectrophotometric techniques.[18, 20] Consequently, research on the degradation products of pharmaceutical PETN should be of significance to the drug industry.

Synthesis of PETN

PETN is generally synthesized by reaction of PE with nitric acid or a nitric-sulfuric acid mixture.[21,22,23] When nitrated with concentrated nitric acid the process is carried out in a stainless steel vessel with agitation at typically 15–25 °C. The PETN product is precipitated by adding sufficient water to the solution to reduce the acid concentration to about 30%. The resulting crystals are first vacuum filtered, then washed with water, next repeatedly washed with a dilute sodium carbonate solution, and finally washed with cold water. Purification is performed by recrystallization that involves dissolving the PETN in acetone containing a small amount of sodium carbonate at 50 °C and reprecipitating with water, which produces a yield of approximately 95%. Bulk PETN is typically shipped in a water–alcohol solution in packaging similar to that used for primary explosives.[24]

A second manufacturing method, the Biazzi continuous process, is also used. In this method the reactants are continuously fed to a series of nitrators at 15–20 °C. Next, the PETN product is separated from the mixture, washed with water and re-dissolved in acetone at 50 °C. This solution is then neutralized with gaseous ammonia, and the PETN is precipitated by dilution with water. The overall yield is more than 95%. In addition, the acetone and the spent acid are readily recovered.[24]

The PE precursor is typically produced via a base-catalyzed reaction of acetaldehyde [75-07-0] with excess formaldehyde [50-00-0]. The aldol condensation of three moles of formaldehyde with one mole of acetaldehyde is followed by a crossed Cannizzaro reaction between PE, the

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19 Stalleicken, D.; Kuntze, U.; Schmid, B.; Hiebl, R.; Ring; J.; Michaelis, K. "Quantitative Determination of Pentaerythrityl Tetranitrate and its Metabolites in Human Plasma by Gas Chromatography/Mass Spectrometry"; *Arzneim.-Forsch./Drug Res.* **1997**, *47*, 347–352.

20 Gupta, V.D.; Gupta, A. "Stability of Some Oral Solid Drug Products when Stored in a Counting Machine"; *Am. J. Hosp. Pharm.* **1979**, *36*, 1539–1541.

21 Desvergnes, L. "Pentaerythritol Tetranitrate or Penthrit"; *Chim. Ind*. **1933**, *29*, 1263-77.

22 Oinuma, S.; Kusakabe, M. "Process for Stabilization of Nitro Compounds"; Jpn. Pat. 51/118 708, 1976.

23 Zeman, S.; Dimun, M.; Cervenka. Z. "Trimethylolmethane derivatives, nitrates"; Czech. Pat. 221 031 B, 1986.

24 Lindner, V. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J.I.; Howe-Grant, M., Eds.;Wiley, New York, 1994; Vol. 10, p. 30.

intermediate product, and formaldehyde to give the final PE product and formate byproduct.[25] These reactions are shown in **Eqs. 1** and **2**.

$$CH_3CHO + 3HCHO \rightarrow C(CH_2OH)_3CHO \quad (1)$$

$$C(CH_2OH)_3CHO + HCHO + NaOH \rightarrow C(CH_2OH)_4 + HCOONa \quad (2)$$

Another PE synthesis route involves reacting formaldehyde with calcium dioxide ($Ca(OH)_2$) [1305-62-0]. The calcium formate ($Ca(CHO_2)_2$) [544-17-2] byproduct is precipitated with oxalic acid [144-62-7].[26]

Impurities in Solid PETN

Commonly reported impurities in PETN include PE, PE-tri-N, PE-di-N, PE-mono-N, dipentaerythritol hexanitrate, (di-PEHN) and tripentaerythritol acetonitrate (tri-PEON). Yasuda reported the identification and determination of three nitrate esters commonly found in manufactured PETN (i.e., PE-tri-N, di-PEHN, and tri-PEON).[27] The separation of PETN and these byproducts were performed on thin-layer chromatography plates and quantified by colormetric reaction and photometry. This technique only identified those species that produce nitrate ions when hydrolyzed with zinc and acetic acid. Therefore, unambiguous identification of all impurities present was not undertaken in this project.

Klassen *et al.* identified several organic salts as impurities in PETN that are byproducts and synthesis aids of PE. These salts, which include formate, acetate and oxalate, were also found to increase under certain accelerated decomposition conditions.[28]

Effect of Impurities

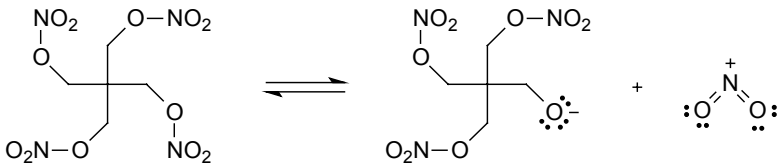
Upon monitoring the heat of fusion value (ΔH_f) determined by calorimetry, Rogers and Dinegar have discovered that disorder within the PETN crystal structure is caused by random inclusions within the lattice of inverted and strained PETN molecules.[2] This disorder results in a decreased ΔH_f. The ΔH_f of a crystalline compound is related to the energy necessary to destroy crystal lattice order. This finding could be significant when considered with the property

25 Berlow, E.; Barth, R.H.; Snow, J.E. *The Pentaerythritols*; Reinhold: NY, 1959; pp 4–24.
26 *Engineering Design Handbook, Properties of Explosives of Military Interest*; AMPC-706-177; Army Material Command: Alexandria, VA, 1971; p. 280.
27 Yasuda, S.K. "Identification and Determination of Impurities in Pentaerythritol Tetranitrate"; *J. Chrom.,* **1970**, *51*, 253–260.

discussed in the beginning of this report, that PETN is not sensitive to shock detonation along one of its crystal axes. PETN could acts as its own "impurity" when it is inverted in the crystal structure. Rogers and Dinegar continued with experiments to determine the effect of impurities on the ΔH_f of the PETN crystal. It was found that small amounts of impurity, less than 1%, had little effect on the value of ΔH_f. Pure PETN had a ΔH_f of 37.0 ± 0.1 cal/g, where as PETN co-crystallized with 1% $^{w}/_{w}$ of the impurity, tri-PEON, had a ΔH_f of 37.0 ± 0.2 cal/g. These values only differ from each other in their uncertainty. Conversely, larger amounts (greater than 2%) of impurities had substantial effects on the ΔH_f. Although researchers conclude that "impurities" in the amounts to be expected in "pure" PETN cannot be responsible for the observed differences in heats of fusion, we do not believe they were aware of all of the impurities in PETN. The ΔH_f of the different crystal habits were measured to be approximately 37, 37 and 32 cal/g, respectively, and were not found to be greatly affected by differences in surface area.

Decomposition of PETN

Aging and accelerated decomposition of PETN has been studied for a variety of formulations and under a number of different temperature and chemical environments. When these studies are considered collectively, we are able to establish a model that describes different decomposition pathways, which become evident when PETN is aged in pure form or in the presence of other chemicals. It is generally accepted that "the decomposition of primary and secondary aliphatic nitrate esters involve the initial, reversible, rate determining scission of the O-NO_2 bond."[29] This scission step is described as a first-order process as shown in **Eq. 3**.



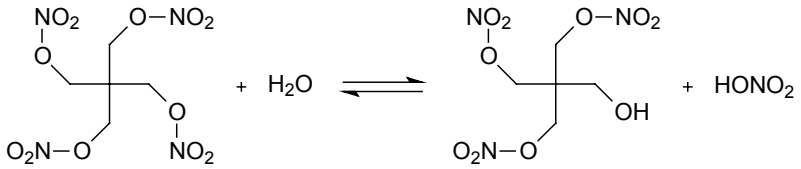
(3)

These decomposition byproducts are relatively reactive. Depending on the conditions, a number of second-order decomposition routes are proposed that involve attack by nitrogen dioxide

28. Klassen, S.E.; Massis, T.M.; Boespflug, E.P.; Montoya; B.M., Reif, J.L. "Ion Chromatography of Energetic Materials at Sandia National Laboratory"; *Thermochim. Acta,* **2001**, *6873*, 1-13.
29 Roos, B.D.; Brill, T.B. "Thermal Decomposition of Energetic Materials 82. Correlations of Gaseous Products with the Composition of Aliphatic Nitrate Esters"; *Combust. Flame*, **2002**, *128*, 181-190.

[10102-44-0] (NO_2). These subsequent decomposition routes are often referred to as autocatalytic or autooxidation reactions. For PETN at ambient temperatures, the possibility for a number of autocatalytic mechanisms involving the oxidation of the PETN alkoxy radical by NO_2 resulting in the formation of either peroxide [$(O_2NOCH_2)_3C\text{-}CH_2OO\cdot$], nitrate [$(O_2NOCH_2)_3C\text{-}NO_2$] or aldehyde [$(O_2NOCH_2)_3C\text{-}CHO$] byproducts exists. The PETN alkoxy radical, although less mobile under low-temperature conditions than NO_2, might also be expected to attack PETN resulting in the formation of polymer-like byproducts (e.g., di-PEHN, and tri-PEON). More extreme temperature conditions above 150 °C yield a variety of decomposition byproducts resulting from further breakdown of PETN.

The presence of other chemicals such as water (a weak nucleophile) apparently promotes a different decomposition pathway. This pathway involves attack of the ester oxygen forming an alcohol group. Because this reaction can occur at each of the nitrate-ester side groups, a stable mono, di, or trinitrated pentaerythritol can be formed. This mechanism proceeds relatively slowly as shown in **Eq. 4**.



(4)

This reaction has been identified in a number of pharmacokinetic studies as mentioned above.[19,20] Although in living systems, hydrolysis is enzymatically facilitated,[30] PETN is readily hydrolyzed in the laboratory.[31] This pathway has been shown to occur under acidic, neutral, and basic conditions. The degradation proceeds sequentially and relatively slowly.

Effect of Temperature on the PETN Physical and Chemical States

Thermal properties and stability of PETN have been studied by many groups. These studies established a consensus regarding temperature-dependent properties that including the melting

30 Kojda, G.; Hacker, A.; Noack, E. "Effects of Nonintermittent Treatment of Rabits with Pentaerythritol Tetranitrate on Vascular Reactivity and Superoxide Production"; Eu. J. Pharmacol. **1998**, *355*, 23-31.
31 Dicarlo, F.J.; Hartigan, J.M.; Phillips, G.E. "Analysis of Pentaerythritol Tetranitrate and Its Hydrolyis Products by Thin Layer Chromatography and Radio Scanning"; *Anal. Chem*. **1964**, *36*, 2301-2303.

point (141.3-143 °C),[9,1] decomposition temperature (163 °C),[32] and activation energy (E_A = 30–70 kcal/mol).[7,33,34,35] These values are determined using a variety of traditional thermal analysis methods that include differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and manometric vacuum stability test (MVST).[11]

The most comprehensive study was performed by Huang *et al.* who conducted DTA, TGA and MVST.[11] The MVST, which measures the amount of gas evolved from a PETN sample in an evacuated container under controlled conditions, reveals a significant rise in gas volume by a factor of approximately three between 110 and 120°C. Furthermore, the MVST curve at 120 °C generated over 40 h conforms to that of an autocatalytic type of reaction. Similar observations were reported earlier by Ng *et al.* who monitored the total pressure of PETN heated under high vacuum.[36] They observed an initial rapid increase in pressure at approximately 75 °C that eventually leveled off at 110 °C, at which point a second rapid increase occurred. Although the initial rapid rise in pressure is attributed to decomposition, others have shown that PETN readily outgasses adsorbed NO_2.[37]

The DTA method compares the temperature of a sample to a standard under a precisely controlled heating curve tested by Huang *et al.*, show two significant thermal points for PETN—an endothermic melting point peak at 141.6 °C and an exothermic decomposition peak at 206.1 °C.[11] The decomposition begins at 155.0°C, but the associated weight loss, as seen by the TGA curve, is relatively low. However, the decomposition increases sharply to a maximum at 206.1°C, which coincides with a weight loss of 92%.

Low-Temperature Decomposition

From the thermal analysis studies of PETN described above, different outgassing or decomposition processes apparently occur above and below approximately 110 °C. For this

32 Ruijuan, X.; Hong, L.; Luo, S.; Liu, J. *Theory Pract. Energ. Mater.,* 3rd Proc. Int. Autumn Semin. Propellants, Explos. Pyrotech.: Chengdu, China, 1999; pp 153–159.
33 Robertson, A.J.B. "Thermal Decomposition of Pentaerythritol Tetranitrate, Nitroglycerin, Ethylenediamine Dinitrate, and Ammonium Nitrate"; *J. Soc. Chem. Ind.* (*London*) **1948**, *67*, 221-4.
34 Andreev, K.K.; Kaidymov, B.I. "Thermal Decomposition of Nitrate Esters. II. Thermal Decomposition of Pentaerythritol Tetranitrate"; *J. Phys. Chem.* **1961**, *35*, 1324.
35 Rogers, R.N.; Morris, E.D. "On Estimating Activation Energies with a Differential Scanning Calorimeter"; *Anal. Chem.* **1966**, *38*, 412-14.
36 Ng; W.L.; Field, J.E.; Hauser, H.M. "Thermal, Fracture, and Laser-Induced Decomposition of Pentaerythritol Tetranitrate"; *J. Appl. Phys.* **1986**, *59*, 3945-52.
37 Volltrauer, H. N. "Real Time Low Temperature Decomposition of Explosives - PETN"; *J. Haz. Mater.* **1982**, *5*, 353-357.

reason is used to delineate between low- and high-temperature phenomenona. In addition, low-temperature accelerated outgassing and decomposition are relevant to shelf-life issues.

The lowest temperature work to date was reported in 1982 by Volltrauer *et al.*[37] This work involved monitoring nitric oxide [10102-43-9] NO and NO_2 from PETN with a chemiluminescence detector. By using a high-sensitivity chemiluminescence NO/NO_x analyzer, they were able to obtain data for samples maintained at temperatures as low as 53 °C. It was noted that when "fresh" PETN is first heated, it evolves more NO_x than when it has been held at a given temperature for several days. Volltrauer *et al.* believe that the "initial" NO_x emission is not the result of decomposition but instead desorption of adsorbed NO_2. As a result, Volltrauer *et al.* report an NO_2 "desorption" activation energy of 15 kcal/mol for both PETN and nitrocellulose (NC). An E_A of approximately 35 kcal/mol was determined from the actual decomposition of PETN between 53 to 120 °C. This later value was determined from NO_x emission upon neglecting the "initial" desorption.

Other low-temperature studies were performed by Kimura of the Japan Defense Agency.[38] In this work, Kimura attempted to understand the so-called PETN autocatalytic decomposition reaction by monitoring luminous emissions from decomposing samples of condensed-phase samples of PETN and NC. It is believed that the autocatalytic reaction proceeds through a complicated series of consecutive free radical intermediates. Kimura supports the consensus that nitrate esters initially decompose by homolytic cleavage of the O-NO_2 bond forming an alkoxy radical and NO_2 as shown in **Eq. 3** above and repeated below. Furthermore, because faint chemiluminescence at the appropriate wavelengths can be observed from PETN and NC, Kimura believes that oxidation is involved in the decomposition process as shown in **Eq. 4**. The pathway to the light emitting step is setup when two peroxy radicals react forming excited state O_2* and RCH=O* as shown in **Eq. 5**. The light-emitting step occurs when two excited state molecules react and emit light as shown in **Eq. 6**.

$$RO\text{-}NO_2 \rightarrow RO\cdot + NO_2 \quad (3)$$

$$RO\cdot + NO_2 \rightarrow ROO\cdot + NO \quad (4)$$

$$2\ ROO\cdot \rightarrow (R'CH{=}O)^* + O_2^* + ROH \quad (5)$$

$$(R'CH{=}O)^* + O_2^* \rightarrow (R'CH{=}O) + O_2 + h\nu \quad (6)$$

Evidence for **Eqs. 4** and **5** was obtained from luminescent-emission spectra data for NC at 150 °C. It was not stated whether this measurement was performed under an air or nitrogen background. From the emission spectra data, emission seen at 510 nm is attributed to the presence of a carbonyl in its first excited triplet state and emissions seen between 560 and 600 nm are associated with electric transitions of singlet oxygen.

From the kinetic scheme shown in **Eqs. 3–6**, Kimura assumes that the rate determining step involves the oxidation of the alkoxy radical (**Eq. 4**). Based on this assumption Kimura calculates an activation energy of 10 and 15 kcal/mol for air and nitrogen, respectively, from emissions between 40 and 90 °C. Kimura supports his interpretation with the studies of Pollard and Wyatt, who report the formation of a peroxy radical ($CH_2COO\cdot$) to be the rate-limiting step of the oxidative reaction (E_A = 15.1 kcal/mol) between formaldehyde and NO_2.[39]

We believe that there may be significance in the similarity between the 15 kcal/mol desorption E_A reported by Volltrauer and the autocatalytic decomposition E_A studied by Kimura. The desorption of adsorbed NO_2 may initiate the autocatalytic decomposition reaction. Furthermore, Volltrauer reports that most of the NO_x produced from PETN at temperatures ranging from 53 to 120 °C is NO_2 (e.g., 80 to 90%), thus suggesting that the amount of reduction of NO_2 to NO by PETN is small in comparison to that of NC. For NC essentially all of the NO_x measured is NO at temperatures above 100 °C.

Klassen *et al.* performed liquid ion chromatographic analysis on liquid extracts from PETN and a formulation of PETN, XTX8003 (see **Table II**), maintained under various environmental and low-temperature (50 to 100 °C) conditions for up to two years.[40] From liquid extraction of PETN, they were able to identify a significant increase in recovered nitrate, formate, acetate, and oxalate anions from PETN maintained at 100 °C for one year compared with that stored under ambient temperatures. These species were extracted by milling the PETN with water in a plastic container using a plastic agitator ball and a Spex 8000 Mixer/Mill. The aqueous mixture was filtered prior to ion exchange liquid chromatography using a dilute sodium hydroxide eluent system. An alternative sonication sample break-up and extraction method was tested. However,

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38 Kimura, J. " Chemiluminescence Study on Thermal Decomposition of Nitrate Esters (PETN and NC)"; *Propellants, Explos. Pyrotech.* **1989**, *14*, 89-92.
39 Pollard, F. H.; Wyatt, M. H. " Reactions between Formaldehyde and Nitrogen Dioxide. I. Kinetics of the Slow Reaction" *Trans. Faraday Soc.* **1949**, *45*, 760-767.

this approach resulted in elevated nitrite levels compared with that from milling extraction lead Klassen *et al.* to conclude that their sonication approach might be accelerating decomposition of PETN.

Nitrate, formate, acetate, and oxalate anion levels were monitored in XTX8003 and PETN (Lot 4330-304M) aged at three different temperatures, 50 ^{o}C, 70 ^{o}C, and 90 ^{o}C, for varying periods of time, for up to two years. The material was further divided into samples that were either protected under a helium atmosphere or exposed to air. Because the elastic nature of XTX8003 prevented efficient milling extraction, a different extraction method was developed and validated by comparing fluoride and chloride anion extraction efficiency with the milling extraction method. A comparison of extraction efficiency was not performed with the acid salts. Sample preparation involved solvent extraction using a 50:50 mixture of acetonitrile [75-05-08] and methanol [57-56-1], which was then evaporated and redissolved with deionized water.

Nitrate anion extracted from the helium protected materials was ≤ 31.4 μg/g as compared with ≤ 73.4 μg/g for materials stored in air. The nitrate-anion response followed approximately a linear relationship as a function of time and temperature. The average level of formate and acetate maintained under helium for two years at 90 °C was much higher for PETN reaching 300-400 μg/g as compared with that of XTX8003, which remained at <15 μg/g. In comparison, the formate and acetate levels in the air-exposed sample peaked at one year at 90 ^{o}C to 55-60 μg/g and then decreased. The oxalate values were even more curious for the investigators. They found that the highest levels for oxalate were produced in the samples aged at 50 ^{o}C for 24 months. This was the case for both helium purged and air-exposed samples. The samples aged at 70 ^{o}C had the next highest oxalate levels, where as the samples aged at 90 ^{o}C had the lowest.

Associating detonation velocity with the abundance of contaminates did not present the anticipated results. Neither a good correlation between detonation velocity and contaminate concentration, nor a defined aging marker could be found. Samples with higher anion levels showed good detonation performance where as samples with lower anion levels showed decreased detonation performance.[28, 40]

Klassen *et al.* are unsure of the mechanisms and kinetics responsible for the formate, acetate and oxalate anions recovered from the heated PETN. The researchers report that oxalate can be

40. Klassen, S. E.; Montoya, B. M.; Boespflug, E. P.; Reif, J. L. "Anion Analysis of Aged XTX8003"; SAND2000-0864, Sandia National Laboratories, Albuquerque, NM, 2000.

present in PETN as a contaminate from the synthetic process, but most of the bulk unaged lots do not contain appreciable amounts of oxalate or other anions.[40] However, it is plausible that these products are synthesis byproducts of the PE and PETN synthesis as described in PETN synthesis section above. Morphological change in addition to decomposition might facilitate the release and extraction of the acid salts if they are ionicly or weakly bound.

High Temperature Decomposition

High-temperature decomposition studies were performed more recently in 1999 by Ruijaun *et al*.[41] This group studied the temperature dependence of PETN decomposition under dry inert conditions ranging from 100-500 °C using pyrolysis GC and MS (PGC/MS) and the Bourdon manometric test. PGS/MS was also equipped for DTA using an instrument developed in-house consisting of an oven pyrolyzer that records the temperature behavior of the sample to a standard over a measured length of time. The sample temperature differs slightly from the standard because the sample experiences thermodynamic events such as molecular rearrangements, outgassing, or changes in state. In addition, the output from the pyrolyzer was analyzed by GC/MS. The MS used was a high-resolution magnetic sector instrument.

Results fell within three characteristic temperature ranges. At the lowest temperature range between 100-130 °C, PETN experienced one outgassing event that produced relatively small quantifies of NO_2 and presumably CH_2O. In the mid-range temperature region from 130 to 250 °C PETN achieves its melting point (141.3 ^oC),[9] the decomposition point (163 ^oC),[32] and auto-detonation point (225 ^oC).[1] Within this range, up to five thermal events and eleven decomposition byproducts were identified. The byproducts include NO_2, CH_2O, N_2O, NO, CO_2, CO, H_2O, CH_3OH, HNO_2, CH_3NO_2, and $(O_2NOCH_2)_3C\text{-}CHO$. The highest range from 250 to 500 ^oC approximates the temperatures experienced by the PETN during an explosion.

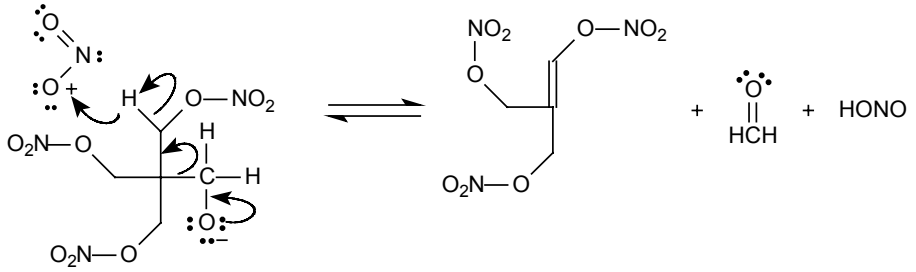
Ruijaun *et al.* describe a different autocatalytic decomposition reaction than Kimura in both the lowest- and second-temperature range of decomposition. Following cleavage of the O-NO_2 bond, Ruijuan *et al.* propose attack of the central carbon by NO_2 resulting in the release of CH_2O as shown in **Eq. 7**. Ruijaun believes that this process is repeated for each nitrate ester side group resulting in the formation of $C(NO_2)_4$, which he identifies in the 250-500 °C range experiments.

41 Ruijuan, X.; Hong, L.; Luo, S.; Liu, J. *Theory Pract. Energ. Mater.,* 3rd Proc. Int. Autumn Semin. Propellants, Explos. Pyrotech.: Chengdu, China, 1999; pp 153–159.

$$(O_2N\text{-}O\text{-}CH_2)_3C\text{-}CH_2O\cdot + NO_2 \rightarrow (O_2N\text{-}O\text{-}CH_2)_3C\text{-}NO_2 + CH_2O \qquad (7)$$

Although the MS resolution did not completely preclude the overlap of NO (m/z 29.998) with nearby CH_2O (m/z 30.011), the CHO (m/z 29.003) fragment ion coincided with the presumed CH_2O response. Unfortunately, NO was not monitored. However, we do not believe these results exclude **Eq. 4** because small quantities of NO have been quantified at low temperatures by Volltrauer.[37]

Because 2-nitro-, 2-[nitroxy(methyl)]-, dinitrate (ester) 1,3-propanediol was not confirmed, it is not clear whether **Eq. 7** is the primary decomposition route. We suggest an alternative route might involve the oxidation of the alkoxy radical shown in **Eq. 4**. NO_2, a strong oxidizing agent, abstracts a hydrogen and resuls in the eventual loss of CH_2O shown in **Eq. 8**.



(8)

Additional oxidation reactions are proposed by Ruijuan *et al.* in the mid-temperature range (130-250 °C), resulting in the formation of further byproducts including $(O_2NOCH_2)_3C\text{-}CHO$.[41] Unfortunately, the presence of this byproduct was not proven because the mass spectral data only revealed fragment ions (the largest being at m/z 116) and not the molecular ion.

Ruijuan *et al.* identified a number of high-temperature (250-500 °C) decomposition byproducts that include $C(NO_2)_4$, CH_2O, NO_2, NO, N_2O, CO_2, CO, CH_4, N_2, CH_3OH, CH_3CN, CHN, H_2O, CH_3NO_2, HNO_2, CH_3COOH, CHOOH, $HOCH_2C{\equiv}CCH_2OH$, $(O_2NOCH_2)_3C\text{-}CHO$, $C(CH_2OH)_4$, $(O_2NOCH_2)_3C\text{-}NO_2$, $(CH_2OH)_3C\text{-}CH_2ONO_2$, and several unknowns.[41] It would appear that the high molecular weight byproducts are produced as the pyrolyzer is heated at a rate of 20 °C/min to its intended isotherm. A follow-up peer-reviewed paper on this work has not yet been published.

The high-temperature decomposition byproducts formed at 210 °C were identified and quantified by Rideal and Robertson using MS and are shown in **Eq. 9**.[42] The residue, which makes up the balance of the decomposition reaction, likely consists of nonvolatile fragments.

$$C_5H_8N_4O_{12} \rightarrow 2.11NO + 0.93CO + 0.52NO_2 + 0.42N_2O + 0.28CO_2 + 0.09H_2 + CH_2O + H_2O + \text{residue} \quad (9)$$

Roos and Brill performed measurments in the range of 250 to 450 °C using specialized Fourier transform infrared (FTIR) and Raman spectroscopy techniques called T-Jump/FTIR and T-Jump/Raman, respectively.[29] T-jump spectroscopy is the interface of a modified, commercial, filament pyrolysis control unit and a spectrometer. Analyses at 450 °C yielded the following decomposition equation.

$$C_5H_8N_4O_{12} \rightarrow 3.083CO + 2.973NO + 2.281H_2 + 1.85O_2 + 0.915CO_2 + 0.416H_2O + 0.339N_2 + 0.307CH_4 + 0.206HCN + 0.193CH_2 + 0.120C_2H_2 + 0.081NO_2 + 0.043HNCO + 0.005N_2O \quad (10)$$

Roos and Brill reported that the balance of the **Eq. 10** formula deviates for C by 1.22%, H by 4.41%, N by 1.73%, and O by 2.15%. Notably, concentrations of the most reactive products (e.g., NO_2 and CH_2O) decrease with increasing temperature.

Hydrolysis of PETN

Although thermal decomposition studies do not readily identify PE and its nitrated congeners, a number of pharmacokinetic studies identify these species as the primary biological metabolites of PETN.[43,44,45] The hydrolysis pathway (**Eq. 4**), which involves chemical attack of

42 Rideal, E.K.; Robertson, A.J.B. " Thermal Decomposition of Pentaerythritol Tetranitrate, Nitroglycerin, Ethylenediamine Dinitrate, and Ammonium Nitrate"; *Proc. R. Soc. London Ser. A* **1948**, *195*, 135.
43 Di Carlo, F.J.; Hartigan, J.M.; Coutinho, C.B.; Coutinho, C.B.; Phillips, G.E. "Absorption, Distribution, and Excretion of Pentaerythritol and Pentaerythritol Tetranitrate by Mice"; *Proc. Soc. Exp. Biol. Med.* **1965**, *118*, 311-15.
44 Crew, M.C.; Coutinho, C.B.; DiCarlo, F.J. "Quantitative Recovery of Radioactivity from Pentaerythritol-14C Tetranitrate Administered to Rats"; *J. Pharm. Sci.* **1966**, *55*, 1137-8.
45 King, S.Y.P.; Fung, H.L. "Rapid Microbial Degradation of Organic Nitrates in Rat Excreta. Re-Examination of the Urinary and Fecal Metabolite Profiles of Pentaerythritol Tetranitrate in the Rat"; *Drug Metab. Disp.* **1984**, *12*, 353-7.

the ester oxygen and thereby forming an alcohol end group, has been shown to occur under acidic, neutral, and basic conditions.[43,46]

An *in vitro* method to produce PETN hydrolysis products has been demonstrated by Basch *et al*.[17] Their procedure involved dissolving PETN in a dioxane-water (82:18) solution and adding 1% by volume concentrated HCl, which was then refluxed for 6 h. This solution was neutralized with $Ca(OH)_2$ and dioxane solution, dried, and then the PE congeners were extracted using ethanol.

Conclusions

An abundance of literature exists regarding the decomposition of PETN that identifies and proposes a number of different mechanisms. Many of these differences, we believe, result from biases imposed by different analytical approaches and environmental conditions under which PETN decomposition is monitored. Nevertheless, a collective review of the literature reveals several distinct mechanisms. Many researchers have identified and acknowledged two primary decomposition routes—one involving cleavage of the O-NO_2 bond followed by a number of proposed autocatalytic decomposition reactions, and the other involving the hydrolysis of the O-NO_2 side group when PETN is decomposed in an aqueous environment.

Scission of the O-NO_2 bond is reported to have an E_A as low as 35 kcal/mole under near-ambient conditions. Although the driving force for this reaction has yet to be addressed, we believe that the interaction of PETN with different reactive residues, which include water, NO_2 and nitrate, formate, acetate and oxalate salts, is the main process. Similarly, we believe that chemical residue from other materials, which might include binders, plasticizers and volatile contaminants, can initiate a decomposition as well.

A number of different autocatalytic reactions have been reported to follow the cleavage of the O-NO_2 bond. Foremost is the attack of the alkoxy radical by NO_2 as described in **Eqs. 4, 5 and 7**. Those compounds that result from such pathways might include $(NO_2OCH_2)_3CCHO$, $(NO_2OCH_2)_2C{=}CHONO_2$, $NO_2OCH{=}C{=}CHONO_2$, $(NO_2OCH_2)_3C\text{-}NO_2$, $(NO_2OCH_2)_2C(NO_2)_2$, $NO_2OCH_2C(NO_2)_3$, and $C(NO_2)_4$. Of these proposed decomposition byproducts, the $(NO_2OCH_2)_3CCHO$ compound has been the only one that has been tentatively identified.

46 Aubertein, P.; Rehling, R. "Hydrolysis of Penthrite (Pentaerythritol Tetranitrate)"; *Mem. Poudres* **1953,** *35*, 91-102.

Furthermore, we believe that other mechanisms involving the attack of PETN by the alkoxy radical, although less mobile than NO_2, result in the formation of polymer-like species such as di-PEHN and tri-PEON that are readily found in PETN.

The importance of chemical environment on the decomposition route becomes self-evident through the hydrolysis reaction of PETN, which is reported as the major decomposition route seen under aqueous environments. In this case, the O-NO_2 bond is broken upon hydrolysis resulting in the formation of PE-mono-N, PE-di-N, and PE-tri-N. Interestingly, these lower nitrate esters of PE are also synthesis byproducts and have not been shown to be a major byproduct formed under anhydrous conditions.

It becomes apparent from different decomposition studies that external conditions such as temperature and chemical environment can influence the diffusion and lifetime of PETN byproducts, NO_2, alkoxy radicals, and other reactive residue, which in return determine the primary decomposition route and rate of PETN.